

A POTENTIAL NUCLEAR MAGNETIC RESONANCE IMAGING
APPROACH FOR NONCONTACT TEMPERATURE MEASUREMENT

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Abstract - It is proposed that in a nuclear magnetic resonance (NMR) imaging experiment that it should be possible to measure temperature through an extended volume. The basis for such a measurement would depend upon sensing a temperature dependent NMR parameter in an inert, volatile molecule (or fluid) filling the volume of interest. Exploratory work suggest that one suitable candidate for such a purpose might be CH_3Cl . Possible parameters, other inert gases and feasible measurement schemes that might provide such temperature measurement will be discussed.

Introduction - For non-contact temperature measurement the predominate approach that has been exploited for many decades has been pyrometry of various sorts. Only now after years of research does it seem that people are finally coming to grips with all aspects of the problem (1). However, the range over which accurate and precise temperature measurements can be made by pyrometry techniques seems to be above about 800K. For the lower temperature region of about 200K to 600K, we would like to suggest a new approach that utilizes the nuclear magnet resonance (NMR) effect.

Some facts about NMR are listed in Figure 1. A great many atomic nuclei are NMR active. The parameters that can be extracted from NMR spectra in many cases reveal fundamental molecular structure data that can only be obtained from other techniques by much more work (2).

The precedent for proposing that temperature measurements can be accomplished in an NMR experiment exists in the multitudes of examples of temperature dependent NMR parameters that have been reported in the last thirty years (3). In Figure 2 are given just two examples. Both these examples were reported sometime ago so that the precision of the exhibited data could probably be improved substantially with present day instrumentation. These examples show that smooth or linear relationships exist for certain NMR parameters over some useful range of temperature (200-500K).

Next let us consider where the NMR effect arises (4). When a mass of NMR active nuclei are placed in a magnet field, a macroscopic magnetization vector results. This vector can be manipulated by radio frequency pulses whose B_1 fields are orthogonal to the B_0 , the main magnetic field. This situation is exhibited and explained in Figure 3. A typical block diagram of a pulse NMR imaging system is shown in Figure 4 (5). In many cases the transmitter and receiver coils are one and the same. In the right side of part a) of the left side of Figure 5 is shown the time dependent signal that would be obtained if the sample contained one chemical type of NMR active nucleus. Fourier transformation of this signal leads to a single line in frequency space. Part b) of this figure shows the situation when there are two chemical types in the sample being studied. In the right side of Figure 5 the principal of how spatial information can be encoded in an NMR experiment by imposing a linear magnetic field gradient is illustrated. The extension of this one dimensional example to two dimensions and three dimensions leads to magnetic resonance imaging (MRI) of a slice or multislices through the sample being investigated. Figure 6 illustrates a typical MRI pulse sequence which involves switching of the three magnetic field gradients and more than one RF pulse (6). The first RF pulse, P4, is a tailored selective $\pi/2$ pulse and the second, P2, is a non-selective π pulse. This pulse sequence is usually repeated during about 120 increments of the Y-gradient. Image reconstruction processing (either Fourier or back-projection) (7) will yield a slice image that exhibits the two dimensional intensity map of some NMR parameter. If the magnitude of the NMR parameter being sensed is temperature dependent then the image maps the temperature in the slice under study.

In the top part of Figure 7 are listed a number of temperature dependent NMR parameters that could be the basis of MRI temperature measurement schemes. In Figure 8 is depicted a possible experimental configuration about a levitation chamber for such a temperature measurement. Although the non-contact temperature scheme needs that prompted this proposal for temperature measurement were in connection with possible deployment about a levitation chamber in zero-g, there are substantial potential applications for such an approach for temperature mapping in all sorts of ground based vessels and pipes containing fluids and gases.

In the bottom part of Figure 7 are listed a few examples of molecules that might be potential candidates on which to base such an MRI temperature measurement scheme. Shown in Figure 9 are some exploratory results with the various chlorinated methanes and some properties of the isotopes ^{35}Cl and ^{37}Cl . It appears that perhaps CH_3Cl might be a possible candidate as a temperature reporting molecule. The NMR spectra of this molecule were

investigated both in the liquid and gas phases but only at one temperature (about 20° C). It should be noted that there is a significant difference between the linewidths in the two phases and also between the ^{35}Cl and ^{37}Cl nuclei. From other work with some other nuclei (8) it is expected that the linewidths of the ^{35}Cl and ^{37}Cl resonances will exhibit changes with temperature. These changes are probably due to modulation of the coupling of the nuclear quadrupole moment with the magnetic dipole moment. The next step in this exploratory work is to characterize in detail the latter temperature dependences both for the liquid and gas phases. There is little data even now on such NMR temperature dependent changes for quadrupolar nuclei. There is even less data on the NMR of gases and their temperature dependencies. Thus, there is a lot of exploratory work to be done before suitable candidates for useful NMR temperature probes can be identified. It is the intention of work in progress to identify several such molecules that will be useful in the temperature range of 200-600K.

In Figure 10 are listed other considerations that bear on the development of this new non-contact temperature approach. The accuracy and precision of ± 3 degrees is a conservative estimate as right now temperature dependent NMR experiments are being done where differences as small as ± 0.5 degrees affect spectra. An important point is that one probably doesn't need high resolution to provide useful temperature mapping. It is usual to acquire NMR images with resolution of 256 x 256 pixels whereas for temperature mapping, grids of 10 x 10 to 50 x 50 may in many cases be totally adequate. There is a tradeoff with resolution and imaging time so lower resolution maps can be obtained with a great saving of time. Another important point is that really high magnetic fields are not necessarily needed to accomplish useful MRI. Excellent proton images are now being obtained at fields as low as 600-2000 gauss. (9,10) Whether satisfactory S/N can be achieved for quadrupolar nuclei with less NMR sensitivity than protons needs to be explored in detail, especially in the gas phase.

Conclusion - A new approach for non-contact temperature measurement has been described above which in the temperature range of 200-600K has the potential to meet the needs of some microgravity and containerless processing experiments. In contrast to the decades of research and development work that have been put in on pyrometry approaches, which have not resulted in many useful instruments for the above mentioned temperature range, it would seem that this new approach has the potential for development into practical protocols and instruments in a period of several years.

References

1. For a recent summary see the contributions in "Noncontact Temperature Measurement," NASA Conference Publication 2503, M.C. Lee Editor, March 1988 and other papers in the present proceedings.
2. See for example, M. L. Martin, J.-J. Delpuech and G. J. Martin, "Practical NMR Spectroscopy," Heyden & Son Ltd, London, 1980.
3. See many examples discussed by J. I. Kaplan and G. Fraenkel in "NMR of Chemical Exchanging Systems," Academic Press, New York, 1980.
4. For a more detailed discussion see reference 2.
5. Figure adapted from P.A. Bottomley, Rev. Sci. Instrum., **53**, 1319 (1982).
6. Reference 5 discusses a number of other pulse sequences.
7. For a review of these techniques see G. T. Herman, "Image Reconstruction from Projections," Academic Press, New York, 1980.
8. S. L. Manatt, unpublished work on ^{14}N and ^{11}B NMR linewidths.
9. H. Lotz, L. Ekelund, S-O. Hietala and G. Wickman, J. Comput. Assist. Tomography, **12**, 1006 (1988).
10. R.E. Sepponen, J.T. Sipponen and A. Sivula, ibid., **9**, 237 (1985).

SOME FACTS:

- FORM OF RADIOFREQUENCY SPECTROSCOPY WITH ATOMIC NUCLEI POSSESSING SPIN (^1H , ^{13}C , ^{31}P , ^{23}Na , ^{15}N , ^2H , ^{17}O , ^{19}F , ETC.)
- REQUIRES MAGNET, R.F. TRANSMITTER-RECEIVER AND DATA ACQUISITION SYSTEM
- AREAS OF NMR SIGNALS ARE USUALLY DIRECTLY PROPORTIONAL TO NUMBER OF NUCLEI SEEN BY PROBE RECEIVER COIL
- FOR A LONG TIME VERY IMPORTANT RESEARCH TECHNIQUE IN BIOLOGY, CHEMISTRY AND PHYSICS AND NOW IMPORTANT IN BIOMEDICINE
- NMR EXPERIMENT CAN BE DONE MANY DIFFERENT WAYS AND CAN YIELD A NUMBER OF DIFFERENT PARAMETERS DIRECTLY RELATED TO MOLECULAR STRUCTURE AND DYNAMICS

Figure 1. Nuclear Magnetic Resonance (NMR): Some Facts

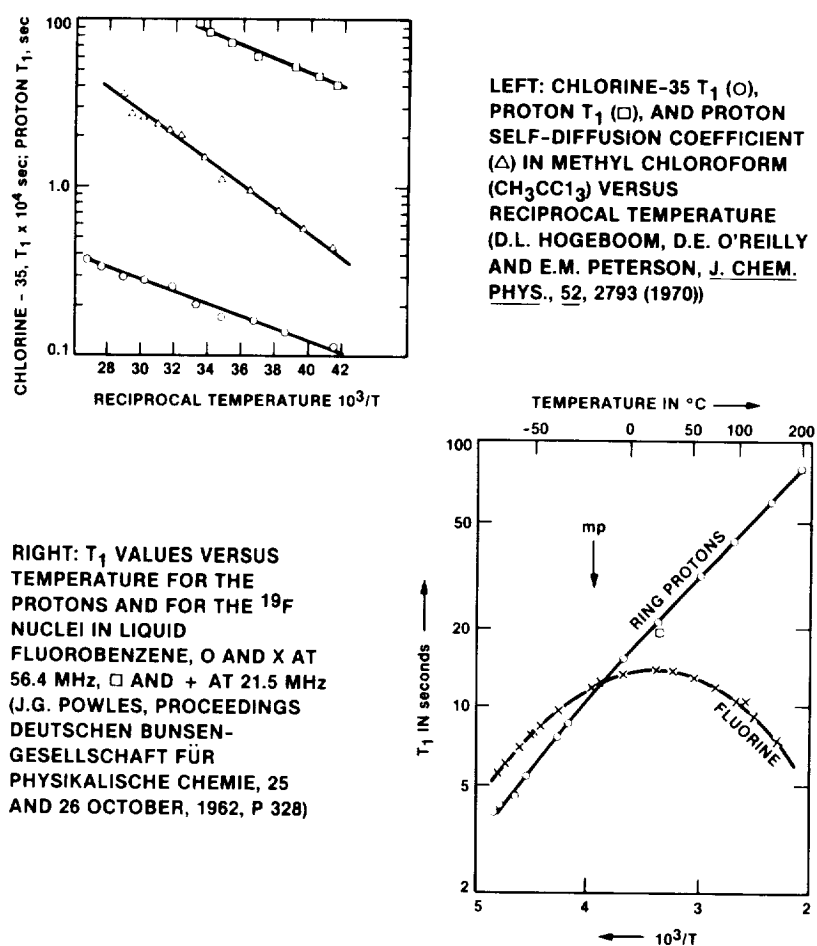


Figure 2. Two Literature Precedents for Proposed NMR Temperature Measurement Approach

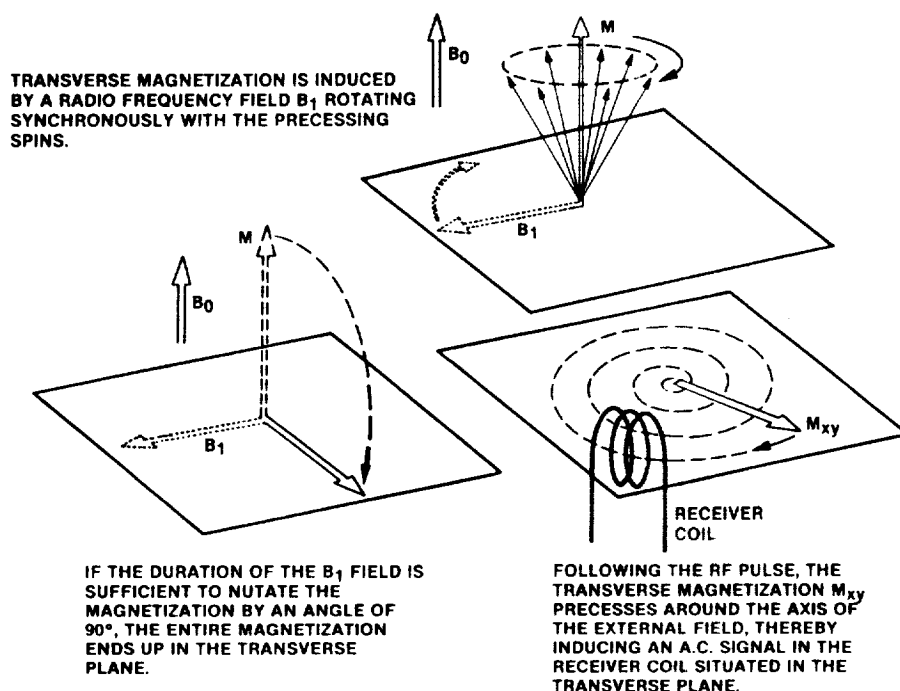


Figure 3. Illustration of How Magnetization Gives Rise to NMR Signal

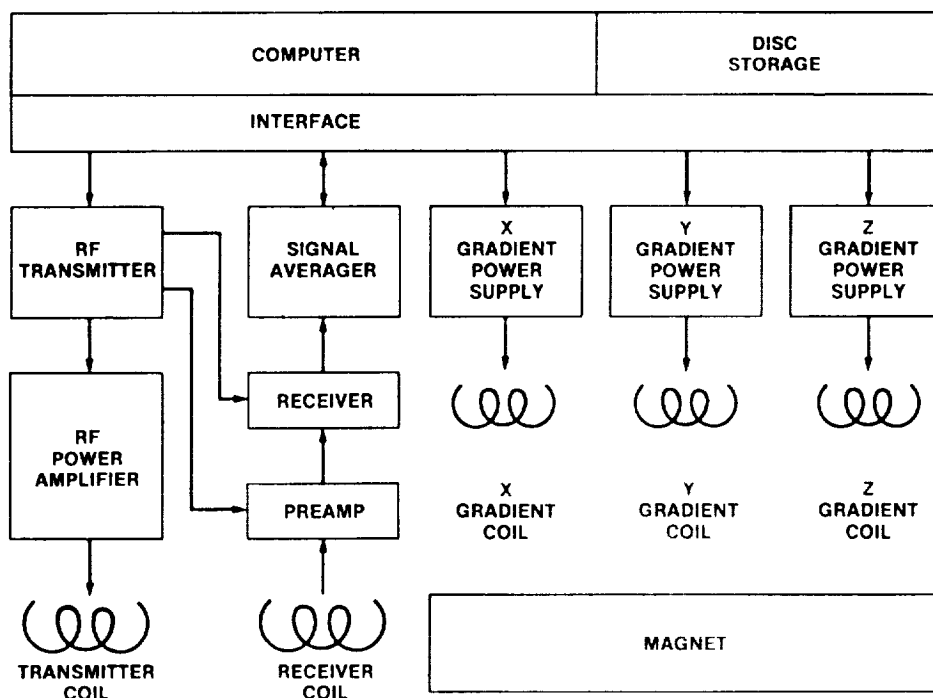


Figure 4. Simplified Block Diagram of a Typical Computer-Based NMR Imaging System; adapted from P. A. Bottomley, *Rev. Sci. Instrum.*, **53**, 1219 (1982)

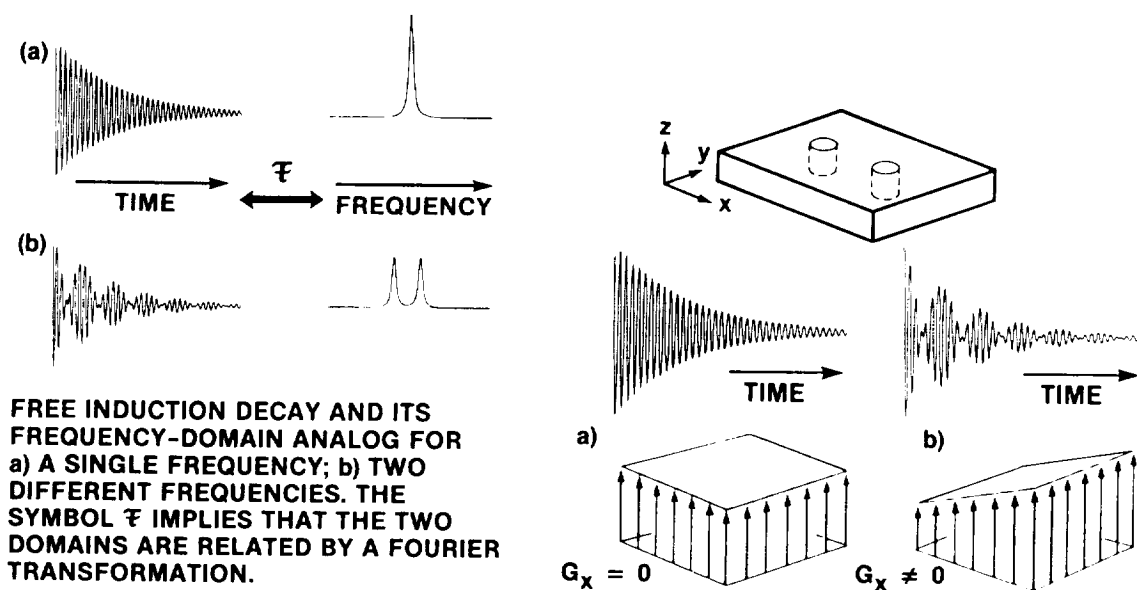


Figure 5. Typical Output From NMR System and Encoding Of Spatial Information By Field Gradient in NMR Experiment

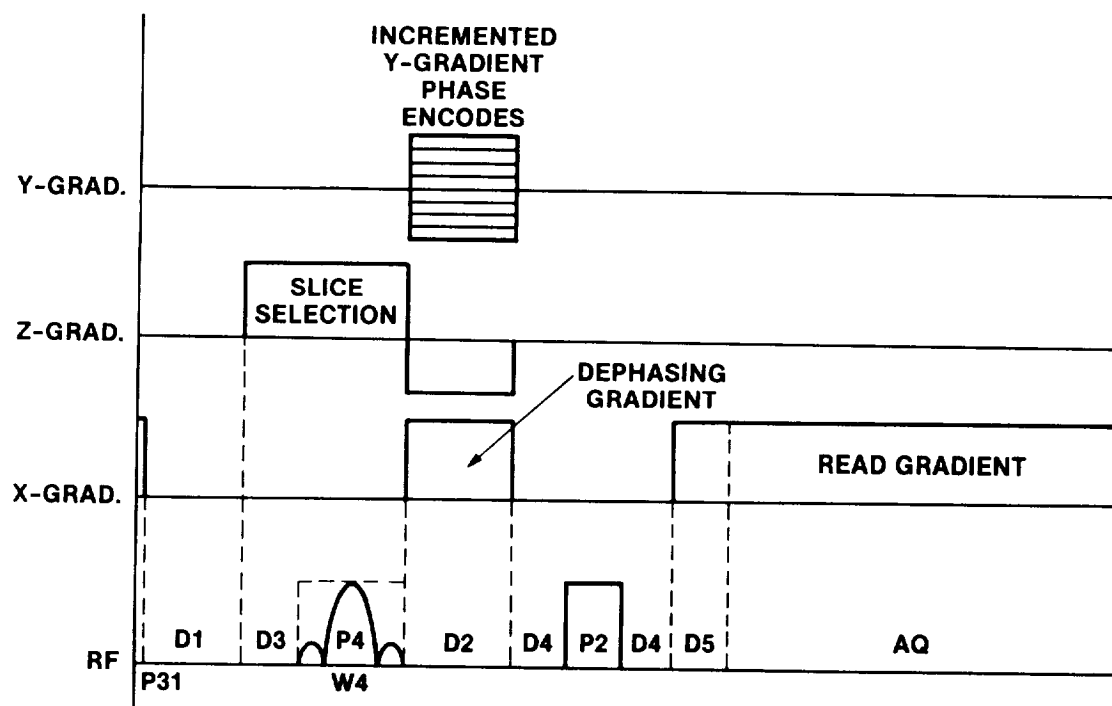


Figure 6. Line Scan Imaging Sequence

NMR PARAMETERS

- T_1 -SPIN LATTICE RELAXATION TIME
- T_2 -SPIN-SPIN RELAXATION TIME
- FOR SPIN > 1 NUCLEI, QUADRUPOLEAR RELAXATION CHANGES
- SLOW MOLECULAR CONFORMATION CHANGES
- COUPLING CONSTANT CHANGES
- CHEMICAL SHIFT CHANGES
- CHEMICAL EXCHANGE EFFECTS

INERT MOLECULES

CClH_3 (^{35}Cl AND ^{37}Cl RESONANCES)

CClF_3 (^{13}C , ^{19}F , ^{35}Cl AND ^{37}Cl RESONANCES)

^{129}Xe AND ^{131}Xe (IN NATURAL ISOTOPIC ABUNDANCES)

$(\text{CH}_3)_3\text{N}$ (^{13}C AND ^{14}N)

CH_3OCH_3 (^{17}O , ENRICHED)

CFD_3 (^2H , ^{13}C AND ^{19}F)

Figure 7. Potential Temperature Dependent NMR Parameters and Some Potential Inert Molecules

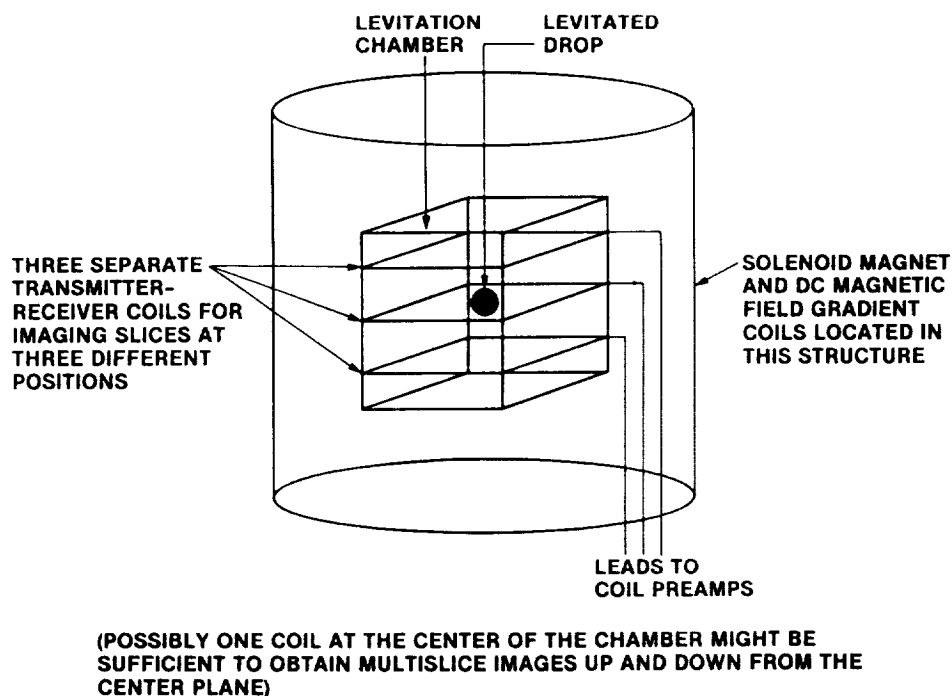


Figure 8. Experimental Configuration

- LINE WIDTHS OF C1 IN CC1₄, CC1₃H, CC1₂H₂ AND CC1H₃ MEASURED
- RATIONAL FOR WORK: PERHAPS TEMPERATURE DEPENDENCE OF LINE WIDTH OF ONE OF THESE MOLECULES MIGHT FORM BASIS FOR TEMPERATURE SCALE

- PROPERTIES OF C1 ISOTOPES

	³⁵ C1	³⁷ C1
SPIN 3/2 ABUNDANCE	75.53%	24.47%
SENSITIVITY RELATIVE ¹ H	4.7 x 10 ⁻³	2.71 x 10 ⁻³
QUADRUPOLE MOMENT	-7.89 x 10 ⁻²⁶ cm ²	-6.21 x 10 ⁻²⁶ cm ²

- RESULTS AT 19.60 MHz FOR ³⁵C1 AND 16.31 MHz FOR ³⁷C1 IN 46.98 x 10³ GAUSS FIELD

	³⁵ C1	³⁷ C1
CC1 ₄	9400 Hz (ℓ)	4400 Hz (ℓ)
CC1 ₃ H	7400 Hz (ℓ)	3700 Hz (ℓ)
CC1 ₂ H ₂	4300 Hz (ℓ)	2300 Hz (ℓ), 3000 Hz (g)
CC1H ₃	1900 Hz (ℓ)	1000 Hz (ℓ), 1500 Hz (g)

- CONCLUSIONS: LINE WIDTHS OF CC1₄, CC1₃H, AND CC1₂H₂ TOO BROAD; CC1H₃ POSSIBLE CANDIDATE FOR DETAILED TEMPERATURE DEPENDENT STUDIES

Figure 9. Preliminary ³⁵C1 and ³⁷C1 NMR Work

- RANGE OF NMR TEMPERATURE MEASUREMENT FROM ABOUT 200-600°K WITH AN ACCURACY OF ± 3 degrees
- PROBABLY ONLY NEED 10 x 10 TO 20 x 20 SLICE IMAGES FOR ADEQUATE TEMPERATURE PROFILES
- ALTHOUGH S/N FOR VARIOUS CANDIDATE GASES AT 1 atm. ARE CALCULATED TO HAVE ADEQUATE S/N FOR MODEST FIELDS, NEED TO EXPLORE SITUATION AT LOWER FIELDS
- MAGNETIC FIELD DOES NOT NEED TO BE HIGH AS GOOD IMAGES HAVE RECENTLY BEEN OBTAINED AT LOW FIELDS (600-2000 GAUSS)
- GROUND-BASED NMR TEMPERATURE PROFILE MEASUREMENT IN CHAMBERS TO BE USED IN SPACE PROCESSING MIGHT BE USEFUL IN ITSELF

Figure 10. Other Considerations